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EP-A- 0 277 003  
EP-A- 0 277 004

JOURNAL OF AMERICAN CHEMICAL SOCIETY, vol. 108, 1986, pages 7410-7411, American Chemical Society; R.F. JORDAN et al.: "Ethylene polymerization by a cationic dicyclopentadienylzirconium(IV) alkyl complex"

(73) Proprietor: **FINA TECHNOLOGY, INC.**  
8350 North Central Expressway  
Dallas, Texas 75206 (US)

(72) Inventor: **Ewen, John A.**  
16615 Kentwood Avenue  
Houston,  
Texas 77058 (US)  
Inventor: **Elder, Michael J.**  
706 Stoneledge  
Friendswood,  
Texas 77546 (US)

(74) Representative: **Leyder, Francis et al**  
c/o Fina Research S.A.  
Zone Industrielle C  
B-7181 Feluy (BE)

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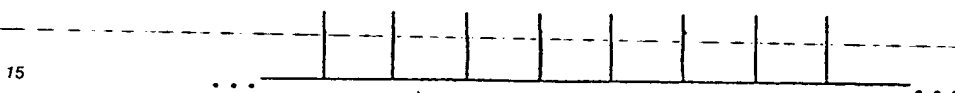
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## Description

## BACKGROUND OF THE INVENTION

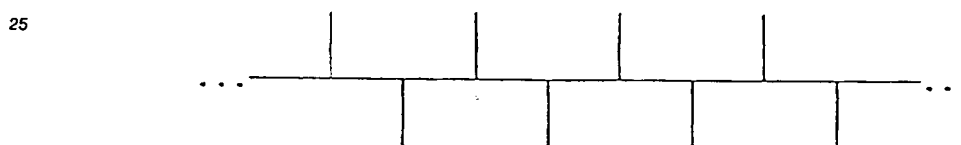
5 FIELD OF THE INVENTION: This invention relates, in general, to a process for preparing catalysts and, specifically, to a process for preparing catalysts for polymerization of olefins.

DESCRIPTION OF RELATED ART: Olefins, especially propylene, may be polymerized to form polyolefins in various forms: isotactic, syndiotactic and atactic. Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic poly-  
 10 propylene may be structurally represented as



Isotactic polypropylene is capable of being a highly crystalline polymer with a high melting point and other desirable physical properties that are considerably different from the polymer in an amorphous  
 20 (noncrystalline) state.

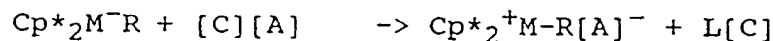
A syndiotactic polymer contains principally units of exactly alternating stereoisomers and is represented by the structure:



A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

35 Polymerization of olefins is primarily with Zeigler-Natta catalysts. One family of Zeigler-Natta catalysts is Group IVB metallocene compounds with methylaluminoxane as a cocatalyst. It has been demonstrated that Zeigler-Natta catalysts for olefin polymerization can be formed by combining a group IVB metallocene with an ionic compound.

40



45

L

Cp\* - pentamethylcyclopentadienyl

M - Group IVB metal

50 R - alkyl

L - ligand

[C] - cation

[A] - anion

The resulting compound is a metallocene cation which acts as a catalyst. The cation [C] of the ionic  
 55 compound reacts with the metallocene to generate an ion pair. The anion, [A], is not coordinated or is only loosely coordinated with the cationic metallocene.

The following methods have been used to produce the above reaction:

One-Electron Oxidation - This method is illustrated in "Ethylene Polymerization by a Cationic

Dicyclopentadienylzirconium(IV) Alkyl Complex", R.F. Jordan, C.S. Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc., p. 7410-7411, Vol. 108 (1986). These early examples used a Lewis base to make the metal cation less electrophilic and  $[BPh_4]^-$  was the anion where Ph is  $C_6H_5$ . The reaction occurred in a coordinating solvent. These catalysts were usually of low activity.

5 Protonation - This method is illustrated by "Synthesis and Insertion Reactions of Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L.M. Wilson, J. Chem. Soc. Commun., p. 1610-1611, (1986); "Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L. Wilson, Organometallics, p. 2556-2563, Vol. 6, (1987); Insertion Reactions of Nitriles in Cationic Alkylbis(cyclopentadienyl)titanium Complexes, M. Bochmann, L. Wilson, Organometallics, p. 1147-1154, Vol. 7 (1987).

10 European Patent Application 0-277-003 relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with a compound having a cation capable of donating a proton and an anion having a plurality of boron atoms. For example, the following reaction illustrates the invention:

15  $\text{bis(cyclopentadienyl)hafnium dimethyl} + \text{N,N-dimethylanilinium bis(7,8-dicarbaundecaborato) cobaltate(III)}$   
 $\rightarrow [Cp_2HfMe][B] + CH_4 + \text{N,N-dimethylaniline}$

where [B] is 7,8-dicarbaundecaborane.

European Patent Application 0-277-004 also relates to work by Turner on a catalyst prepared by a  
 20 protonation method. A bis(cyclopentadienyl) metal compound is combined with an ionic compound having a cation which will irreversibly react with a ligand on the metal compound and an anion having a plurality of lipophilic radicals around a metal or metalloid ion. For example, the following reaction illustrates the invention:

25  $\text{tri(n-butyl)ammonium tetra(pentafluorophenyl)boron} + \text{bis(cyclopentadienyl)zirconium dimethyl}$   
 $\rightarrow [Cp_2ZrMe][BPh_4] + CH_4 + \text{tri(n-butyl)N}$

A by-product of the protonation reaction is a Lewis base (amine) some of which can coordinate to the cations and thus inhibit catalyst activity. Starting materials must be chosen carefully to avoid generating  
 30 particular amines which are catalyst poisons. In addition, the catalyst and the polymer produced with this catalyst contains undesirable and toxic residual amines.

Ligand abstraction - The ligand abstraction method is illustrated in "Multiple Metal-Carbon Bonds", R. R. Schrock, P. R. Sharp, J. Am. Chem. Soc., p. 2389-2399, Vol. 100, No. 8 (April, 2, 1978).

In most known processes, methylaluminoxane (MAO) is added with the metallocene compound to act  
 35 as a cocatalyst. The function of MAO is to initiate the alkylation and promote ionization of the metallocene compound. The cocatalyst is a scavenging agent which reduces the poisons which decrease catalyst activity. Present known processes require a large excess of MAO to be added. MAO has the disadvantage of being relatively expensive. This results in high costs for the catalyst system.

#### 40 SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for making an improved catalyst for polymerization of olefins.

And, it is an object of this invention to provide a process for making a catalyst with relatively high  
 45 activity.

Also, it is an object of this invention to synthesize metallocene cations with no Lewis base as a side product.

Further, it is an object of this invention to eliminate the necessity to choose starting materials to control the by-products which may be produced as catalyst poisons.

50 Additionally, it is an object of this invention to eliminate methylaluminoxane (MAO) as a cocatalyst in polymerization of polypropylene.

Moreover, it is an object of this invention to produce polymers which are free of aluminum oxide.

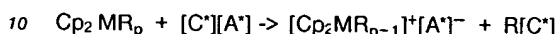
As well, it is an object of this invention to produce a polymer which is free of undesirable and toxic amines.

55 These and other objects are accomplished by mixing an ionizing agent, such as triphenylcarbenium tetrakis(pentafluorophenyl)boronate, with neutral derivatives of metallocenes and adding the mixture to an olefin.

## DESCRIPTION OF THE INVENTION

The invention is for a process of producing a catalyst for polymerization of olefins by ionizing a metallocene with an ionizing agent which does not contain an active proton and which has an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene. The anion is also chemically unreactive with the cation.

In the new synthesis procedure the ionizing ionic compound is mixed with neutral derivatives of metallocenes producing the following reaction:

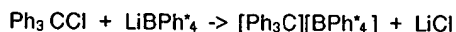


where Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group IIIB, IVB, VB or VIB metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except that if R is a hydride only one R is a hydride; p is from 1 to 4, C<sup>+</sup> is a carbonium, oxonium or sulfonium cation and A<sup>-</sup> is an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene and is chemically unreactive with [Cp<sub>2</sub>MR<sub>p-1</sub>]<sup>+</sup>.

Each reactant is placed in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation. Examples of such solvents are toluene and methylene chloride. The preferred solvent is toluene. The two reactants are dissolved separately in the same solvent and are mixed together at room temperature at a mole ratio ranging from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound. A preferred mole ratio is from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound. The most preferred mole ratio is 1 mole of metallocene : 1 mole of ionizing compound. After mixing, the mixture is added to an olefin under conditions to effect polymerization. The preferred olefins are ethylene and propylene, the most preferred being propylene.

An ionic compound containing a carbonium, oxonium or sulfonium ion, such as triphenylcarbenium tetrakis(pentafluorophenyl)boronate, is mixed with a neutral derivative of a metallocene. Triphenylcarbenium tetrakis(pentafluorophenyl)boronate acts as an ionizing agent which ionizes the metallocene. A cationic metallocene catalyst is formed.

Triphenylcarbenium tetrakis(pentafluorophenyl)boronate [Ph<sub>3</sub>C][BPh<sub>4</sub><sup>-</sup>] is produced by the following reaction:



where Ph is phenyl and Ph<sup>\*</sup> is pentafluorophenyl. Triphenylcarbenium is a cation. Tetrakis(pentafluorophenyl) boronate is an anion.

Triphenylcarbenium tetrakis(pentafluorophenyl)boronate was produced with the following laboratory method. A bright yellow solution of 27.1 mmoles of Ph<sub>3</sub>CCl in 150 cc of methylene chloride was added dropwise at 25°C to 25 gm of LiB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> slurried in 350 cc of methylene chloride. The orange slurry was stirred for 30 minutes and then filtered. The solids containing [Ph<sub>3</sub>C][BPh<sub>4</sub><sup>-</sup>] and LiCl were washed with methylene chloride. The combined wash and filtrate was concentrated to 75 cc and then cannulated into 400 cc of pentane with rapid stirring. The solids were washed several times with pentane and small amounts of toluene until a bright yellow powder of [Ph<sub>3</sub>C][BPh<sub>4</sub><sup>-</sup>] was obtained. The yield was 20 grams (75%).

The neutral derivative of a metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group IIIB, IVB, VB or VIB metal, preferably a Group IV metal, such as titanium, hafnium or zirconium, most preferably zirconium for higher catalyst activity and hafnium for higher molecular weight, R is a hydride, a halogen, an amide or a hydrocarbyl radical such as an alkyl, aryl, alkenyl, alkylaryl or arylalkyl radical having from 1 to 20 carbon atoms, each R being the same or different, except that if R is a hydride only one R is a hydride and p is from 1 to 4. The preferred neutral derivatives of metallocene are ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl and isopropylidene(cyclopentadienyl-1-fluorenyl)zirconium dimethyl. The most preferred neutral derivative of metallocene is ethylene bis(indenyl)zirconium dimethyl.

Polymerization of the olefin is accomplished by any of the known means for polymerization of olefins with metallocene catalysts, for example polymerization in bulk, slurry or gas phase. For polypropylene, polymerization temperatures range from -80 °C to 150 °C, preferably 25 °C to 90 °C and most preferably from 50 °C to 80 °C.

5 The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

#### 10 EXAMPLE I

55 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 5 cc of toluene. 40 mg of Et(IndH<sub>4</sub>)<sub>2</sub>ZrMe<sub>2</sub> was dissolved in 5 cc of toluene. The two solutions were mixed together for 5 minutes at room temperature, giving a clear yellow solution.

15 The mixture was added by syringe to a 2 liter Zipperclave reactor. 1.0 liter of propylene was added to the reactor. Reactor temperature was set to 70 °C. The contents of the reactor were agitated. The temperature remained at 70 °C during the sixty minute polymerization period after which propylene was vented from the reactor. The contents of the reactor were washed with acetone and dried in a vacuum oven.

The polymer was analyzed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

#### EXAMPLE II

25 The procedure of Example I was repeated using 40 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 20 mg of Et(IndH<sub>4</sub>)<sub>2</sub>ZrMe<sub>2</sub>. The results are shown in Table I.

#### EXAMPLE III

30 The procedure of Example I was repeated using 30 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 15 mg of Et(IndH<sub>4</sub>)<sub>2</sub>ZrMe<sub>2</sub>. The reactor temperature was set at 80 °C and the temperature remained at 80 °C. The results are shown in Table I.

#### EXAMPLE IV

35 The procedure of Example I was repeated using 60 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of Et(IndH<sub>4</sub>)<sub>2</sub>ZrMe<sub>2</sub>. Reactor temperature was set at 50 °C and the temperature remained at 100 °C. Run time was 10 minutes. The results are shown in Table I.

#### EXAMPLE V

40 The procedure of Example I was repeated using 55 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 50 mg of Et(IndH<sub>4</sub>)<sub>2</sub>ZrMe<sub>2</sub>. Reactor temperature was set at 50 °C and increased to 168 °C. Run time was 10 minutes. The results are shown in Table I.

#### 45 EXAMPLE VI

The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. Reactor temperature was set at 50 °C and the temperature remained at 50 °C. The results are shown in Table I.

#### 50 EXAMPLE VII

The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The temperature was set at 50 °C and remained at 50 °C. The results are shown in Table I.

## EXAMPLE VIII

The procedure of Example I was repeated using 120 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 80 mg of  $i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$ . Reactor temperature was set at 70 °C and the temperature increased above 100 °C. The results are shown in Table I.

## EXAMPLE IX

The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of  $i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$ . Reactor temperature was set at 70 °C and the temperature increased to 78 °C. The results are shown in Table I.

## EXAMPLE X

The procedure of Example I was repeated using 60 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 40 mg of  $i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$ . Reactor temperature was set at 70 °C. The results are shown in Table I.

The following results are from the experimental runs described above using the method of the present invention.

TABLE I

| RUN # | CATALYST, + mg                             | IONIZING AGENT, + + mg                  | TIME, min. |
|-------|--------------------------------------------|-----------------------------------------|------------|
|       | $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$  | $[\text{Ph}_3\text{C}][\text{BPh}_4^-]$ |            |
| 1     | 40                                         | 55                                      | 60         |
| 2     | 20                                         | 40                                      | 60         |
| 3     | 15                                         | 30                                      | 80         |
| 4     | 50                                         | 60                                      | 10         |
| 5     | 50                                         | 55                                      | 10         |
|       | $\text{Et}(\text{Ind})_2\text{ZrMe}_2$     | $[\text{Ph}_3\text{C}][\text{BPh}_4^-]$ |            |
| 6     | 60                                         | 100                                     | 60         |
| 7     | 60                                         | 100                                     | 30         |
|       | $i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$ | $[\text{Ph}_3\text{C}][\text{BPh}_4^-]$ |            |
| 8     | 80                                         | 120                                     | 5          |
| 9     | 60                                         | 100                                     | 60         |
| 10    | 40                                         | 60                                      | 60         |

+  $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$  = Ethylenebis(tetrahydroindenyl)zirconium dimethyl

$\text{Et}(\text{Ind})_2\text{ZrMe}_2$  = Ethylenebis(indenyl)zirconium dimethyl

$i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$  = isopropylidene (cyclopentadienyl-1-fluorenyl) zirconium dimethyl

+ +  $[\text{Ph}_3\text{C}][\text{BPh}_4^-]$  = triphenylcarbenium tetrakis(pentafluorophenyl)boronate.



| RUN # | TEMP, °C | YIELD, gm | Melting Temp °C |
|-------|----------|-----------|-----------------|
| 1     | 70       | 9         | 138             |
| 2     | 50       | 55        | 138             |
| 3     | 80       | 45        | 131             |
| 4     | 50*      | 74        | 134             |
| 5     | 50*      | 135       | -               |
| 6     | 50       | 19        | 137             |
| 7     | 50       | 11        | 134             |
| 8     | 70*      | 224       | 115             |
| 9     | 70**     | 51        | -               |
| 10    | 70***    | 186       | 119             |

\*Runaway reaction; peak reaction temperature >100 °C

\*\*Exotherm; peak reaction temperature 78 °C

\*\*\*Exotherm

The process described by this invention synthesizes cations which are used as catalysts in olefin polymerization. The process of making catalysts with this invention produces catalysts having high activity and does not produce by-products which can inhibit catalyst activity. This new synthesis is a clean reaction which does not produce a Lewis base. The process generates active catalysts by removing a methyl anion from a group IVB metallocene derivative.

#### Claims

##### 1. A process for making a catalyst comprising:

- mixing an ionizing ionic compound with a neutral derivative of a metallocene; and
- allowing contact between the ionizing ionic compound and the neutral derivative of a metallocene such that the metallocene is ionized by the ionizing ionic compound and an ion pair is formed in which the metallocene cation acts as a catalyst;

wherein the neutral derivative of a metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group IIIB, IVB, VB or VIB metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except that if R is a hydride only one R is a hydride and p is from 1 to 4;

wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and

wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.

##### 2. A process as recited in Claim 1 wherein, before mixing, the ionizing ionic compound is dissolved in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation.

##### 3. A process as recited in Claim 2 wherein, before mixing the neutral derivative of a metallocene is separately dissolved in the same solvent.

##### 4. A process as recited in Claim 3 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound.

##### 5. A process as recited in Claim 4 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound.

6. A process as recited in Claim 5 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges is 1 mole of metallocene : 1 mole of ionizing compound.
7. A process as recited in Claim 4 wherein the metal is a Group IVB metal chosen from the group consisting of titanium, zirconium and hafnium.
8. A process as recited in Claim 7 wherein the metal is hafnium.
9. A process as recited in Claim 7 wherein the metal is zirconium.
10. A process as recited in Claim 9 wherein R is a hydrocarbyl radical chosen from the group consisting of an alkyl radical, an aryl radical, an alkenyl radical, an alkylaryl radical and an arylalkyl radical having from 1 to 20 carbon atoms.
11. A process as recited in Claim 10 wherein the neutral derivative of a metallocene is chosen from the group consisting of ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
12. A process as recited in Claim 11 wherein the neutral derivative of a metallocene is ethylenebis(indenyl)zirconium dimethyl.
13. A process as recited in Claim 12 wherein the ionic compound is triphenylcarbenium tetrakis(pentafluorophenyl) boronate.
14. A process as recited in Claim 13 wherein the solvent is toluene.
15. A process for polymerization of an olefin comprising:
  - a) mixing an ionizing ionic compound with a neutral derivative of a metallocene;
  - b) allowing contact between the ionizing ionic compound and the neutral derivative of a metallocene such that the metallocene is ionized by the ionizing ionic compound and an ion pair is formed in which the metallocene cation acts as a catalyst; and
  - c) contacting the catalyst with the olefin under conditions to effect polymerization; wherein the neutral derivative of a metallocene is of the general formula:
 
$$\text{Cp}_2\text{MR}_p$$

wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group IIIB, IVB, VB or VIB metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only that if R is a hydride one R is a hydride and p is from 1 to 4;

wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and

wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.
16. A process as recited in Claim 15 wherein, before mixing, the ionic compound is dissolved in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation.
17. A process as recited in Claim 16 wherein, before mixing, the neutral derivative of a metallocene is dissolved in the same solvent.
18. A process as recited in Claim 17 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound.
19. A process as recited in Claim 18 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound.

20. A process as recited in Claim 19 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges is 1 mole of metallocene : 1 mole of ionizing compound.
21. A process as recited in Claim 18 wherein the metal is a Group IVB metal chosen from the group consisting of titanium, zirconium and hafnium.
22. A process as recited in Claim 21 wherein the metal is hafnium.
23. A process as recited in Claim 21 wherein the metal is zirconium.
24. A process as recited in Claim 23 wherein R is a hydrocarbyl chosen from the group consisting of an alkyl radical, an aryl radical, an alkenyl radical, an alkylaryl radical and an arylalkyl radical having from 1 to 20 carbon atoms.
25. A process as recited in Claim 24 wherein the neutral derivative of a metallocene is chosen from the group consisting of ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
26. A process as recited in Claim 25 wherein the neutral derivative of a metallocene is ethylene bis(indenyl)zirconium dimethyl.
27. A process as recited in Claim 26 wherein the ionic compound is triphenylcarbenium tetrakis(pentafluorophenyl) boronate.
28. A process as recited in Claim 27 wherein the solvent is toluene.
29. A process as recited in Claim 28 beginning at a reaction temperature which ranges from -80 °C to 150 °C.
30. A process as recited in Claim 29 beginning at a reaction temperature which ranges from 25 °C to 90 °C.
31. A process as recited in Claim 30 beginning at a reaction temperature which ranges from 50 °C to 80 °C.

# Patentansprüche

## 1. Verfahren zum Herstellen eines Katalysators, umfassend:

- Mischen einer ionisierenden Ionenverbindung mit einem neutralen Derivat eines Metallocens und
- Gestatten des Kontaktes zwischen der ionisierenden Ionenverbindung und dem neutralen Derivat eines Metallocens derart, daß das Metallocen durch die ionisierende Ionenverbindung ionisiert und ein Ionenpaar gebildet wird, in dem das Metallocen-Kation als ein Katalysator wirkt, worin das neutrale Derivat eines Metallocens die allgemeine Formel hat:



worin Cp eine Cyclopentadienyl- oder eine substituierte Cyclopentadienylgruppe ist, jedes Cp gleich oder verschieden ist, M ein Metall der Gruppe IIIB, IVB, VB oder VIB ist, R ein Hydrid-, ein Halogen-, ein Amid- oder ein Kohlenwasserstoffrest ist, jedes R gleich oder verschieden ist, ausgenommen daß, wenn R ein Hydrid ist, nur ein R ein Hydrid ist, und p hat einen Wert von 1 bis 4,

worin die ionisierende Ionenverbindung kein aktives Proton enthält und ein Carbonium-, Oxonium- oder Sulfonium-Kation enthält, und

worin das Anion der ionisierenden Ionenverbindung nicht koordinativ oder nur lose koordinativ an das Metallocen-Kation gebunden ist und mit dem Metallocen-Kation chemisch nicht reagiert.

## 2. Verfahren nach Anspruch 1, worin vor dem Vermischen die ionisierende Ionenverbindung in einem Lösungsmittel gelöst wird, die mit dem Metallocen-Kation nicht koordinativ oder nur lose koordinativ

gebunden ist.

3. Verfahren nach Anspruch 2, worin vor dem Vermischen das neutrale Derivat eines Metallocens separat im gleichen Lösungsmittel gelöst wird.
- 5 4. Verfahren nach Anspruch 3, worin das Molverhältnis des neutralen Derivats eines Metallocens zur Ionenverbindung im Bereich von 10 Molen von Metallocen : 1 Mol der ionisierenden Verbindung bis 1 Mol von Metallocen : 10 Mole der ionisierenden Verbindung liegt.
- 10 5. Verfahren nach Anspruch 4, worin das Molverhältnis des neutralen Derivats eines Metallocens zur Ionenverbindung im Bereich von 2 Molen von Metallocen : 1 Mol der ionisierenden Verbindung bis 1 Mol Metallocen : 2 Mole der ionisierenden Verbindung liegt.
- 15 6. Verfahren nach Anspruch 5, worin das Molverhältnis des neutralen Derivats eines Metallocens zur Ionenverbindung 1 Mol Metallocen : 1 Mol der ionisierenden Verbindung beträgt.
7. Verfahren nach Anspruch 4, worin das Metall ein Metall der Gruppe IVB ist, ausgewählt aus der Gruppe bestehend aus Titan, Zirkonium und Hafnium.
- 20 8. Verfahren nach Anspruch 7, worin das Metall Hafnium ist.
9. Verfahren nach Anspruch 7, worin das Metall Zirkonium ist.
- 25 10. Verfahren nach Anspruch 9, worin R ein Kohlenwasserstoffrest ist, ausgewählt aus der Gruppe bestehend aus einem Alkylrest, einem Arylrest, einem Alkenylrest, einem Alkarylrest und einem Aralkylrest mit 1 bis 20 Kohlenstoffatomen.
- 30 11. Verfahren nach Anspruch 10, worin das neutrale Derivat eines Metallocens ausgewählt ist aus der Gruppe bestehend aus Ethylen-bis(tetrahydroindenyl)zirkoniumdimethyl, Ethylen-bis(indenyl)-zirkoniumdimethyl und Isopropyliden-(cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl.
12. Verfahren nach Anspruch 11, worin das neutrale Derivat eines Metallocens Ethylen-bis(indenyl)-zirkoniumdimethyl ist.
- 35 13. Verfahren nach Anspruch 12, worin die Ionenverbindung Triphenylcarbenium-tetrakis(pentafluorphenyl)-boranat ist.
14. Verfahren nach Anspruch 13, worin das Lösungsmittel Toluol ist.
- 40 15. Verfahren zum Polymerisieren eines Olefins, umfassend:
  - a) Vermischen einer ionisierenden Ionenverbindung mit einem neutralen Derivat eines Metallocens und
  - b) Gestatten des Kontaktes zwischen der ionisierenden Ionenverbindung und dem neutralen Derivat eines Metallocens derart, daß das Metallocen durch die ionisierende Ionenverbindung ionisiert und ein Ionenpaar gebildet wird, in dem das Metallocen-Kation als ein Katalysator wirkt, und
  - 45 c) in Berührung bringen des Katalysators mit dem Olefin unter Bedingungen, um Polymerisation zu bewirken,

worin das neutrale Derivat eines Metallocens die allgemeine Formel hat:

$$\text{Cp}_2\text{MR}_p$$

worin Cp eine Cyclopentadienyl- oder eine substituierte Cyclopentadienylgruppe ist, jedes Cp gleich oder verschieden ist, M ein Metall der Gruppe IIIB, IVB, VB oder VIB ist, R ein Hydrid-, ein Halogen-, ein Amid- oder ein Kohlenwasserstoffrest ist, jedes R gleich oder verschieden ist,

55 ausgenommen daß, wenn R ein Hydrid ist, nur ein R ein Hydrid ist, und p hat einen Wert von 1 bis 4,

worin die ionisierende Ionenverbindung kein aktives Proton enthält und ein Carbonium-, Oxonium- oder Sulfonium-Kation enthält, und

worin das Anion der ionisierenden Ionenverbindung nicht koordinativ oder nur lose koordinativ an das Metallocen-Kation gebunden ist und mit dem Metallocen-Kation chemisch nicht reagiert.

16. Verfahren nach Anspruch 15, worin vor dem Vermischen die ionisierende Ionenverbindung in einem Lösungsmittel gelöst wird, die mit dem Metallocen-Kation nicht koordinativ oder nur lose koordinativ gebunden ist.
17. Verfahren nach Anspruch 16, worin vor dem Vermischen das neutrale Derivat eines Metallocens separat im gleichen Lösungsmittel gelöst wird.
18. Verfahren nach Anspruch 17, worin das Molverhältnis des neutralen Derivats eines Metallocens zur Ionenverbindung im Bereich von 10 Molen von Metallocen : 1 Mol der ionisierenden Verbindung bis 1 Mol von Metallocen : 10 Mole der ionisierenden Verbindung liegt.
19. Verfahren nach Anspruch 18, worin das Molverhältnis des neutralen Derivats eines Metallocens zur Ionenverbindung im Bereich von 2 Molen von Metallocen : 1 Mol der ionisierenden Verbindung bis 1 Mol Metallocen : 2 Mole der ionisierenden Verbindung liegt.
20. Verfahren nach Anspruch 19, worin das Molverhältnis des neutralen Derivats eines Metallocens zur Ionenverbindung 1 Mol Metallocen : 1 Mol der ionisierenden Verbindung beträgt.
21. Verfahren nach Anspruch 18, worin das Metall ein Metall der Gruppe IVB ist, ausgewählt aus der Gruppe bestehend aus Titan, Zirkonium und Hafnium.
22. Verfahren nach Anspruch 21, worin das Metall Hafnium ist.
23. Verfahren nach Anspruch 21, worin das Metall Zirkonium ist.
24. Verfahren nach Anspruch 23, worin R ein Kohlenwasserstoffrest ist, ausgewählt aus der Gruppe bestehend aus einem Alkylrest, einem Arylrest, einem Alkenylrest, einem Alkarylrest und einem Aralkylrest mit 1 bis 20 Kohlenstoffatomen.
25. Verfahren nach Anspruch 24, worin das neutrale Derivat eines Metallocens ausgewählt aus der Gruppe bestehend aus Ethylen-bis(tetrahydroindenyl)zirkoniumdimethyl, Ethylen-bis(indenyl)zirkoniumdimethyl und Isopropyliden(cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl.
26. Verfahren nach Anspruch 25, worin das neutrale Derivat eines Metallocens Ethylen-bis(indenyl)-zirkoniumdimethyl ist.
27. Verfahren nach Anspruch 26, worin die Ionenverbindung Triphenylcarbenium-tetrakis(pentafluorphenyl)-boronat ist.
28. Verfahren nach Anspruch 27, worin das Lösungsmittel Toluol ist.
29. Verfahren nach Anspruch 28, das bei einer Reaktionstemperatur beginnt, die im Bereich von -80 °C bis 150 °C liegt.
30. Verfahren nach Anspruch 29, das bei einer Reaktionstemperatur beginnt, die im Bereich von 25 °C bis 90 °C liegt.
31. Verfahren nach Anspruch 30, das bei einer Reaktionstemperatur beginnt, die im Bereich von 50 °C bis 80 °C liegt.

#### Revendications

1. Procédé pour la préparation d'un catalyseur comprenant :
  - a) mélanger un composé ionique ionisant avec un dérivé neutre de métallocène; et

b) permettre le contact entre le composé ionique ionisant et le dérivé neutre de métallocène de telle sorte que le métallocène soit ionisé par le composé ionique ionisant et qu'une paire d'ion soit formée dans laquelle le cation métallocène agit en tant que catalyseur;  
dans lequel le dérivé neutre de métallocène a la formule générale :



où Cp est un cyclopentadiényle ou un groupe cyclopentadiényle substitué, chaque Cp étant identique ou différent, M est un métal du groupe IIIB, IVB, VB ou VIB, R est un hydruure, un halogène, une amine ou un radical hydrocarboné, chaque R étant identique ou différent, sauf si R est un hydruure auquel cas un R seulement est un hydruure et p vaut de 1 à 4;

dans lequel le composé ionique ionisant ne contient pas de proton actif et contient un cation carbonium, oxonium ou sulfonium; et

dans lequel l'anion du composé ionique ionisant n'est pas ou est seulement faiblement coordonné au cation métallocène et est chimiquement non réactif avec le cation métallocène.

2. Procédé selon la revendication 1 dans lequel, avant mélange, le composé ionique ionisant est dissous dans un solvant qui n'est pas ou est seulement faiblement coordonné au cation métallocène.

3. Procédé selon la revendication 2 dans lequel, avant mélange, le dérivé neutre de métallocène est dissous séparément dans le même solvant.

4. Procédé selon la revendication 3 dans lequel le rapport molaire du dérivé neutre de métallocène au composé ionique va de 10 moles de métallocène : 1 mole de composé ionisant jusqu'à 1 mole de métallocène : 10 moles de composé ionisant.

5. Procédé selon la revendication 4 dans lequel le rapport molaire du dérivé neutre de métallocène au composé ionique va de 2 moles de métallocène : 1 mole de composé ionisant jusqu'à 1 mole de métallocène : 2 moles de composé ionisant.

6. Procédé selon la revendication 5 dans lequel le rapport molaire du dérivé neutre de métallocène au composé ionique est ce 1 mole de métallocène : 1 mole de composé ionisant.

7. Procédé selon la revendication 4 dans lequel le métal est un métal du groupe IVB choisi parmi le groupe constitué du titane, du zirconium et de l'hafnium.

8. Procédé selon la revendication 7 dans lequel le métal est l'hafnium.

9. Procédé selon la revendication 7 dans lequel le métal est le zirconium.

10. Procédé selon la revendication 9 dans lequel R est un radical hydrocarboné choisi parmi le groupe consistant en un radical alkyle, aryl, alkényle, alkylaryl ou arylalkyl ayant de 1 à 20 atomes de carbone.

11. Procédé selon la revendication 10 dans lequel le dérivé neutre de métallocène est choisi parmi le groupe consistant en l'éthylène bis(tétrahydroindényle)zirconium diméthyle, l'éthylènebis(indényle)zirconium diméthyle et l'isopropylidène(cyclopentadiényle-1-fluorényle)zirconium diméthyle.

12. Procédé selon la revendication 11 dans lequel le dérivé neutre de métallocène est l'éthylènebis(indényle)zirconium diméthyle.

13. Procédé selon la revendication 12 dans lequel le composé ionique est le triphénylcarbénium tétrakis(pentafluorophényle)boronate.

14. Procédé selon la revendication 13 dans lequel le solvant est le toluène.

15. Procédé pour la polymérisation d'une oléfine comprenant :

a) mélanger un composé ionique ionisant avec un dérivé neutre de métallocène;

b) permettre le contact entre le composé ionique ionisant et le dérivé neutre de métallocène de telle sorte que le métallocène soit ionisé par le composé ionique ionisant et qu'une paire d'ion soit formée dans laquelle le cation métallocène agit en tant que catalyseur;

c) contacter le catalyseur avec l'oléfine dans des conditions pour effectuer la polymérisation;

5 dans lequel le dérivé neutre de métallocène a la formule générale :



10 où Cp est un cyclopentadiényle ou un groupe cyclopentadiényle substitué, chaque Cp étant identique ou différent, M est un métal du groupe IIIB, IVB, VB ou VIB, R est un hydruure, un halogène, une amine ou un radical hydrocarboné, chaque R étant identique ou différent, sauf si R est un hydruure auquel cas un R seulement est un hydruure et p vaut de 1 à 4;

dans lequel le composé ionique ionisant ne contient pas de proton actif et contient un cation carbonium, oxonium ou sulfonium; et

15 dans lequel l'anion du composé ionique ionisant n'est pas ou est seulement faiblement coordonné au cation métallocène et est chimiquement non réactif avec le cation métallocène.

16. Procédé selon la revendication 15 dans lequel, avant mélange, le composé ionique est dissous dans un solvant qui n'est pas ou est seulement faiblement coordonné au cation métallocène.

20 17. Procédé selon la revendication 16 dans lequel, avant mélange, le dérivé neutre de métallocène est dissous dans le même solvant.

25 18. Procédé selon la revendication 17 dans lequel le rapport molaire du dérivé neutre de métallocène au composé ionique va de 10 moles de métallocène : 1 mode de composé ionisant jusqu'à 1 mode de métallocène : 10 moles de composé ionisant.

30 19. Procédé selon la revendication 18 dans lequel le rapport molaire du dérivé neutre de métallocène au composé ionique va de 2 moles de métallocène : 1 mole de composé ionisant jusqu'à 1 mode de métallocène : 2 modes de composé ionisant.

20. Procédé selon la revendication 19 dans lequel le rapport molaire du dérivé neutre de métallocène au composé ionique est de 1 mole de métallocène : 1 mole de composé ionisant.

35 21. Procédé selon la revendication 18 dans lequel le métal est un métal du groupe IVB choisi parmi le groupe constitué du titane, du zirconium et de l'hafnium.

22. Procédé selon la revendication 21 dans lequel le métal est l'hafnium.

40 23. Procédé selon la revendication 21 dans lequel le métal est le zirconium.

24. Procédé selon la revendication 23 dans lequel R est un radical hydrocarboné choisi parmi le groupe consistant en un radical alkyle, aryl, alkényle, alkylaryl ou arylalkyl ayant de 1 à 20 atomes de carbone.

45 25. Procédé selon la revendication 24 dans lequel le dérivé neutre de métallocène est choisi parmi le groupe consistant en l'éthylène bis(tétrahydroindényle)zirconium diméthyle, l'éthylènebis(indényle)-zirconium diméthyle et l'isopropylidène(cyclopentadiényle-1-fluorényle)zirconium diméthyle.

50 26. Procédé selon la revendication 25 dans lequel le dérivé neutre de métallocène est l'éthylènebis(indényle)zirconium diméthyle.

27. Procédé selon la revendication 26 dans lequel le composé ionique est le triphénylcarbénium tétrakis(pentafluorophényle)boronate.

55 28. Procédé selon la revendication 27 dans lequel le solvant est le toluène.

29. Procédé selon la revendication 28 commençant à une température de réaction qui s'échelonne de -80 °C à 150 °C.

30. Procédé selon la revendication 29 commençant à une température de réaction qui s'échelonne de 25 °C à 90 °C.

5 31. Procédé selon la revendication 30 commençant à une température de réaction qui s'échelonne de 50 °C à 80 °C.

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